
Transparent Spinel Fabricated from Novel Powders: Synthesis, Microstructure and Optical Properties¹

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ABSTRACT

Magnesium aluminate spinel powders have been synthesized from boehmite by a unique method in which Mg²⁺ ions are metal exchanged into the boehmite surfaces. Excellent control over the starting particle size, size distribution, purity and stoichiometry of the Mg-doped boehmite powder is possible by this method. The microstructures as well as the optical properties of dense, hot-pressed spinel are examined with the goal of better understanding the overall densification mechanisms and how they relate to the amount of LiF added to promote densification. Extreme sensitivity of the microstructure and transparency to the purity of the starting powders is shown.

INTRODUCTION

Military demand for transparent ceramics has weapon system designers seeking window and dome materials with excellent broadband transparency that are erosion-resistant in variable environments at high speeds and are inexpensive enough for single-use munitions. Single crystal sapphire serves as the baseline material in many of these systems; however, its cost remains prohibitively high for many high-volume applications.

Requirements for transparent armor differ from those for windows and domes but have been equally challenging; the material must be lightweight, suffer minimal visual distortion after sustaining multiple localized hits, and be night vision compatible among other requirements [1]. Common applications for transparent armor include personnel

¹ Distribution is unlimited.

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protection in the form of face shields and visors, windows for ground vehicles such as HUMVEES and armored cars, and windshields and lookdown windows for aircraft. Spinel (MgAl_2O_4), ALON, and sapphire are the leading candidates for these applications [2,3], and developmental efforts are underway in all three materials to meet the demand for increasingly larger components (4-7).

Magnesium aluminate spinel (MgAl_2O_4) is a ceramic with a cubic crystal structure characterized by magnesium ions tetrahedrally coordinated with oxygen and aluminum octahedrally coordinated with oxygen. A unit cell contains 32 oxygen ions, 16 octahedral cations, and 8 tetrahedral cations. The generic form of spinel is AB_2O_4 where A are divalent ions such as Zn, Cd, Mg, Fe, Mn, Ni, or Co and the B are trivalent ions like Al or Fe. Most varieties of spinel are not transparent and are known more for their magnetic properties. MgAl_2O_4 however, in its pure polycrystalline form, can be processed into transparent optically isotropic components. Spinel is transparent to electromagnetic radiation from the ultraviolet through the mid-infrared (0.2 to 5.5 microns). As depicted in Figure 1, spinel has a distinct transmission advantage over sapphire and ALON from 4.5 to 5.5 μm , a region of particular importance for seeker and electro-optic imaging systems. Optical scatter is generally very low due to spinel's cubic crystal structure; however, porosity and impurities at grain boundaries can increase both scatter and absorption.

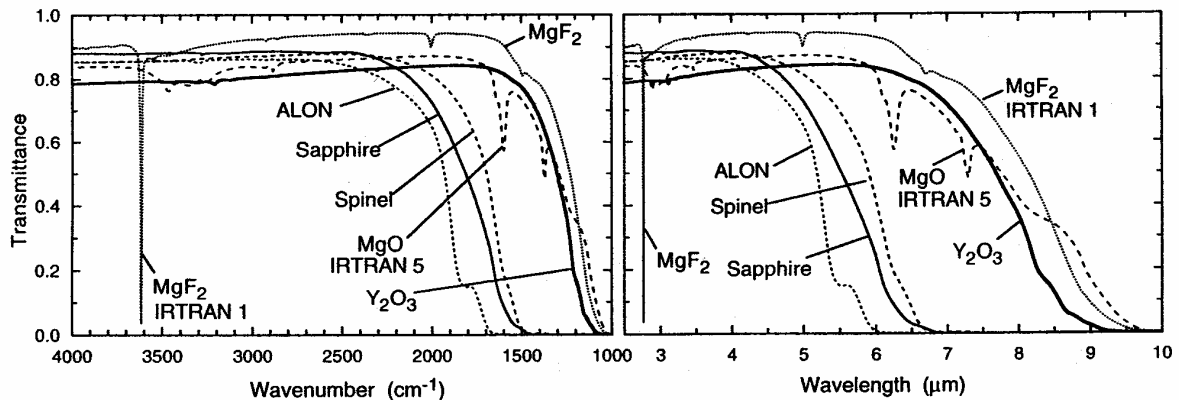


Figure 1. Transmission spectra for infrared materials. Reproduced from [8].

In processing of polycrystalline, transparent spinel, the volume fraction of second phases and porosity must be minimized. Though high-quality transparent spinel has been produced successfully [2-4], the densification mechanisms, and in particular the role of LiF as a sintering aid is still not well understood. During the last several years, much higher purity starting powders of spinel have become available so that better control over impurity levels is possible. The present study describes experiments that are designed to understand how LiF contributes to late stage sintering of spinel.

EXPERIMENTAL TECHNIQUES

Powder Preparation

The MgAl_2O_4 powders used to prepare transparent spinel parts were produced in a three step, single pot process [9,10]. The first step was the hydrolysis of aluminum sec-butoxide ($\text{Al}(\text{CH}_3\text{CH}(\text{O})\text{CH}_2\text{CH}_3)_3$) (ASB, Chattem Chemicals) to produce a boehmite sol. ASB from Chattem Chemicals is a liquid at room temperature and has less than 5ppm impurities. Hydrolysis of the ASB was carried out in 80 °C distilled water. At 80 °C, the kinetically stable hydrolysis product is boehmite (i.e., $\text{Al}(\text{O})\text{OH}$) instead of gibbsite, $\text{Al}(\text{OH})_3$, that forms by hydrolysis of ASB at lower temperatures. After hydrolysis was started the mixture was peptized using a carboxylic acid. Additional acid was then added to convert the nanosized boehmite particles to carboxylate-surface-modified boehmite nanoparticles. The mixture was heated overnight and then $\text{Mg}(\text{acac})_2$ was added to the reaction mixture along with additional water. One set of spinel powders was synthesized from ultra-high purity $\text{Mg}(\text{acac})_2$ which did not contain parts per million impurities that the less pure $\text{Mg}(\text{acac})_2$ contained. As shown below, this had a dramatic result on the transparency. The reaction mixture was then stirred for an additional two hours at 80 °C wherein the magnesium from the $\text{Mg}(\text{acac})_2$ exchanges with aluminum at the boehmite surface. The exchanged Al^{3+} forms aluminum acetylacetonate. The resulting mixture was then cooled to room temperature and spray-dried. This process produces a fine white powder with a high surface area of $\sim 250 \text{ m}^2/\text{g}$ and is indistinguishable from boehmite by XRD analysis.

The spray-dried Mg-doped boehmite powders were then heated to produce the MgAl_2O_4 powders for use in hot-press experiments. Heating the carboxylate-surface-modified boehmite powders to temperatures exceeding 500 °C causes the loss of the carboxylic acid at ~ 300 °C and transformation of the Mg-doped boehmite into Mg-doped γ -alumina by loss of water (e.g., $2\text{Al}(\text{O})\text{OH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$) at temperatures above 500 °C. No significant additional transformation of the Mg-doped Al_2O_3 after 900 °C is observed by XRD analysis. Further heating of the powders to above 900 °C in air results in the complete transformation of the Mg-doped alumina powders to MgAl_2O_4 . At 1000 °C, the powders have a relatively high surface area of $\sim 77 \text{ m}^2/\text{g}$, while additional heating to 1200 °C reduces the surface area to $24 \text{ m}^2/\text{g}$.

Hot Pressing

Spinel powders were mixed with LiF (ranging from 0.0 to 1.0 wt%), by dry-tumbling the powders in a polyethylene bottle containing high purity alumina mixing balls. The powders were densified in a Thermal Technology Inc. (model number 610G-25T) hot press. A graphite die (diameter 25.4 mm) fixture was used with graphite foil as a liner. A pre-load of 3.5 MPa was applied prior to heating. The specimens were heated at about 2 °C/min to 1550 °C and held for 2 hrs. A uniaxial die pressure of 35 MPa was applied at about 1550 °C. During the entire run a vacuum better than 10^{-5} Torr, was maintained. Subsequent to hot pressing, some specimens were exposed to heat treatments at 1550 °C in air for 10 and 50 hrs. The objective of the heat treatments was to examine microstructural evolution.

Characterization

Specimens were cut to a uniform thickness of 1.25 mm, except for one highly transparent specimen that was cut to a thickness 2.2 mm. Specimens were polished to 1 μm or below with diamond polishing media. Transmissivity measurements were made with a Varian 5G Spectrophotometer at wavelengths 300–1400 nm. Reflectivity measurements were made on the best specimen with the same equipment. Microstructure characterization of the hot-pressed spinel samples was performed by fracturing specimens in a vice and observing by scanning electron microscopy (SEM), using a FEI Quanta600 instrument operating at 30 kV. In order to minimize electrostatic charging under the electron beam, samples were gold-coated (SEM).

RESULTS

Transmissivity

Transmissivity results for dense, polished spinel specimens with varying LiF content are shown in Figure 2. The lowest transmissivity was observed for undoped spinel (0.0 wt. % LiF), and the transmissivity generally increased with an increase in LiF, except that specimens doped with 0.50 wt. % LiF were less transparent than those doped with 0.25 wt. % LiF. Most remarkable however is the specimen fabricated with ultra high purity powder and doped with 1.00 wt. % LiF. The average transmissivity of this specimen is above 85 %; reflectivity was measured to be between 13 and 15 % depending on wavelength, and thus the absorption of the specimen is nearly zero. It is also noted that the specimen thickness (2.2 mm) is nearly twice that of the other specimens. The specimen is shown in the inset.

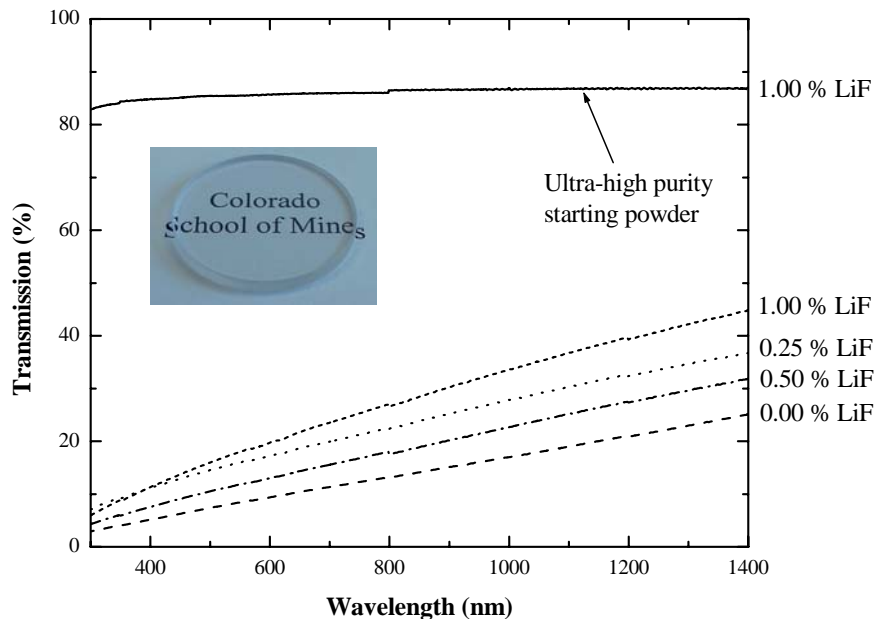


Figure 2. Transmissivity data for spinel specimens containing varying amounts of LiF sintering aid. The highest transmissivity was achieved using the ultra-high purity

powder; the corresponding hot pressed specimen (2.2mm thick) is shown in the inset. Surface reflectivity measured for this specimen was about 13-15 %.

Microstructure

Representative microstructures of the as hot pressed spinel with 0.0 and 1.0 wt. % LiF sintering aid are shown in Figure 3. Figures 3a and 3b show specimens made with normal powder, whereas Figure 3c shows the specimen made with the ultra-high purity powder. Spinel that contained 1.0 wt. % LiF, made with normal powder exhibits a much finer grain size (approximately 10–20 μm grain diameter), compared with that containing no LiF (approximately 10–50 μm grain diameter). It is also apparent that a higher amount of transgranular fracture occurs in this sample compared to that with LiF. A transgranular region of fracture is shown in the central region of Figure 3a. The microstructure of spinel made with ultra-high purity powder is remarkable different (Figure 3c). First, the grain size (approximately 40–100 μm grain diameter) is much larger than that in the spinel made with normal powder. Second, the fracture surface, which is nearly completely intergranular, reveals that the grain boundaries are not faceted, but contain a much higher degree of curvature. Finally, no pores were observed in any region of the specimen, even at higher magnification.

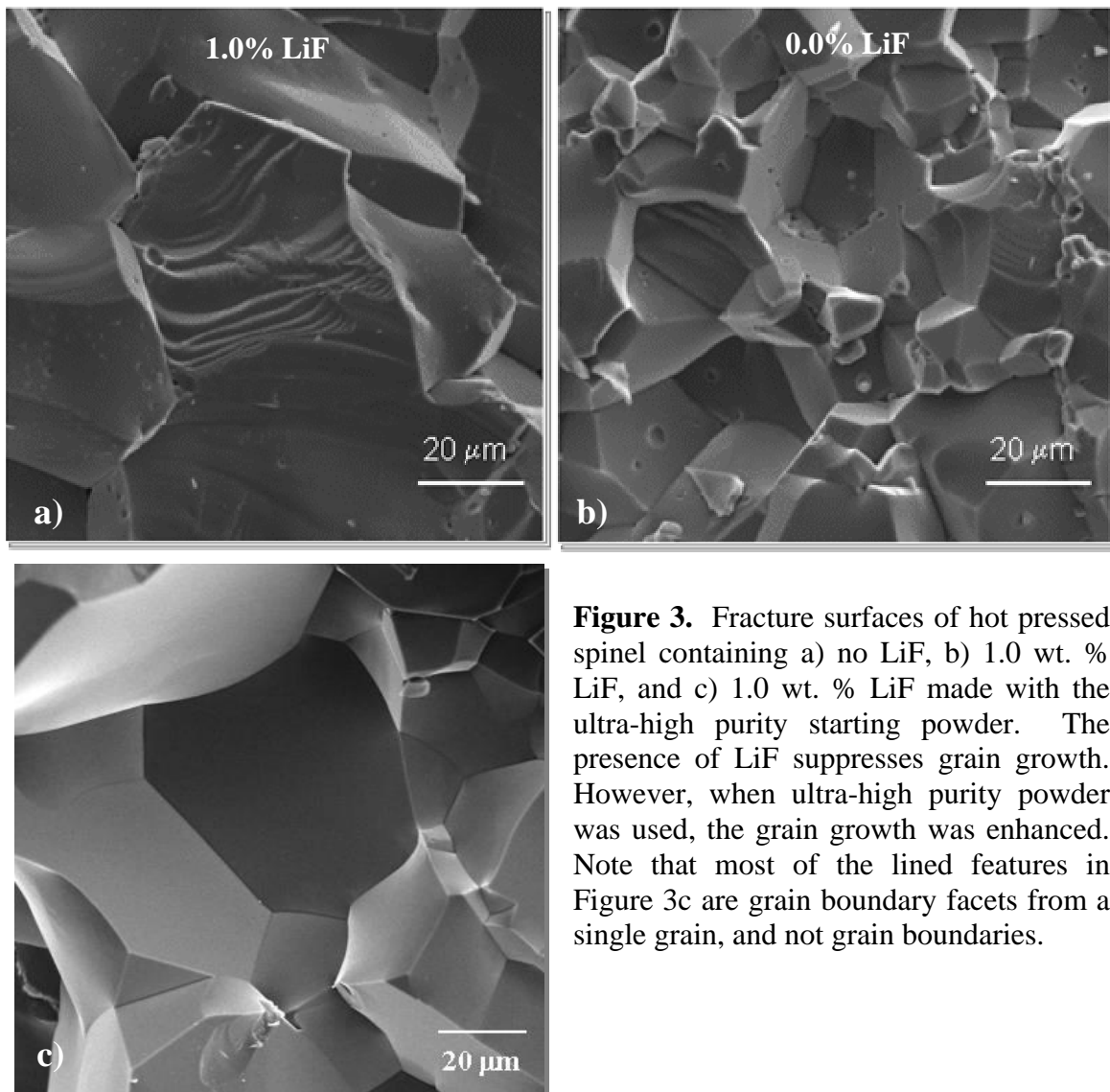


Figure 3. Fracture surfaces of hot pressed spinel containing a) no LiF, b) 1.0 wt. % LiF, and c) 1.0 wt. % LiF made with the ultra-high purity starting powder. The presence of LiF suppresses grain growth. However, when ultra-high purity powder was used, the grain growth was enhanced. Note that most of the lined features in Figure 3c are grain boundary facets from a single grain, and not grain boundaries.

Though all specimens fabricated were measured to be 99-100 % dense within experimental error, spinel that contained no LiF exhibited a larger number of fine pores, consistent with its low transmissivity (Figure 2). The pores in all specimens were always located at the grain boundary regions (Figure 4). No pores were observed in any of the transgranular regions of the fracture surfaces, indicating that no pores were trapped within grains. Many of the grain triple junction regions (arrow in lower portion of Figure 4) contained elongated pores indicative of pore coalescence.

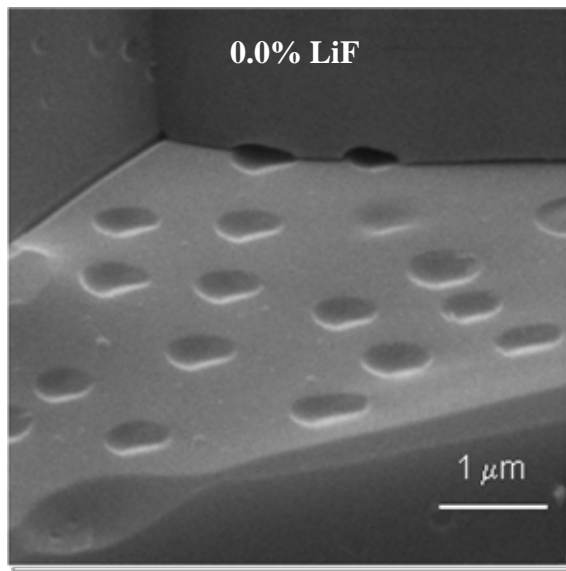


Figure 4. Fracture surface of as-hot pressed spinel that contains no LiF, revealing that pores are located along grain boundaries. The arrow indicates a region where pores have coalesced at the junction of three or more grains.

Specimens that experienced heat treatment from 10 to 50 hrs at 1550 °C in air did not exhibit a change in grain size. However, subsequent to the heat treatment, the specimens became white and lost any transparency. A remarkable change was observed in the pore arrangement. Extensive pore coalescence occurred in all specimens, but was more extensive in spinel without LiF. Figure 5 shows the microstructures of specimens annealed for 10 hrs.

DISCUSSION

There may be two reasons that the presence of LiF in the starting powders influences the hot pressed grain size in spinel (compare Figures 3a and 3b). First, it is possible that the densification kinetics are altered such that grain growth occurs at a much slower rate. Grain boundary mobility has been observed to be sensitive to the stoichiometry of spinel [11,12], which in turn may be influenced by the presence of LiF. This is however unlikely because, if grain growth was simply slowed, the heat treatments of 10 and 50 hrs at 1550 °C should have resulted in an increase of grain size. A second, more likely reason that LiF influences grain size is that it alters the thermodynamic driving force for grain growth. Specifically, the presence of LiF may lower the grain boundary energy. Though LiF was not detected by analytic methods in SEM or in transmission electron

microscopy studies [13], the quantities may be below detection limits. It may also be that its presence during sintering alters the grain boundary structure or chemistry in such a way that the grain boundary energy is lowered. It is unlikely that the presence of LiF alters the effect of grain boundary drag by pores, as has been noted when MgO is added as a sintering aid to make translucent Al_2O_3 [14]. If this were the case, then undoped

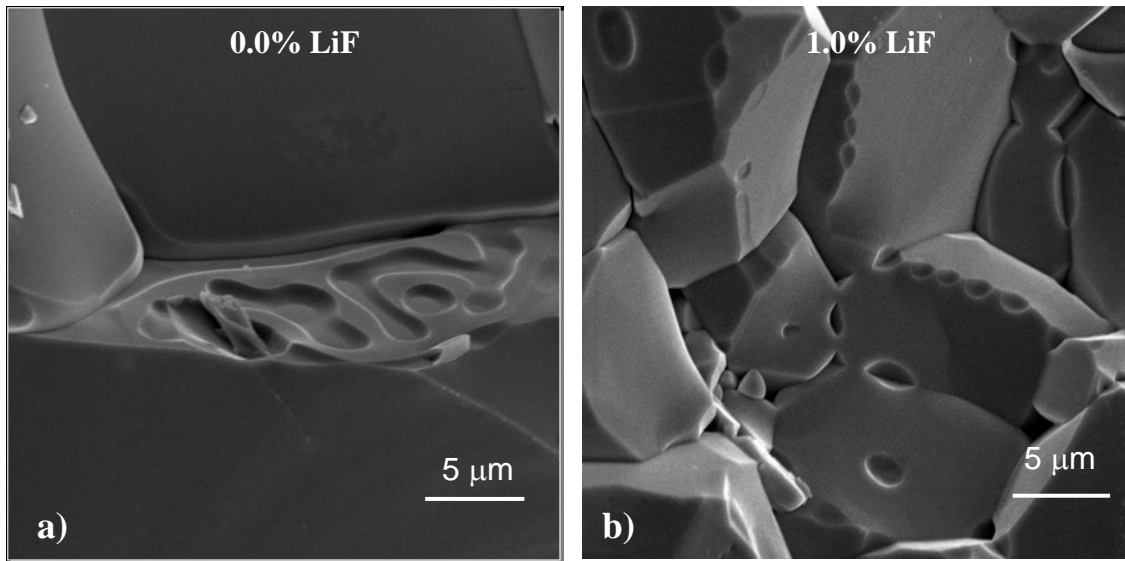


Figure 5. Fracture surface of spinel specimens annealed at 1550°C for 10 hrs. When LiF is not added as a sintering aid, Fig. 5a, then pore coalescence is much more extensive than when LiF is added, Fig. 5b. Pore faceting is also observed, and is more abundant in the spinel without LiF. The grain size did not change as a result of heat treatment.

spinel specimens would contain pores within the grains. The present observations of the lack of porosity on transgranular fracture surfaces of undoped spinel indicates that all the pores are located on grain boundaries. Therefore, the effect of LiF must be to alter the grain boundary energy directly. The relative surface to grain boundary energies may also be important in the microstructural evolution, and these may change when LiF is present. It is further likely that the effect of LiF is modified in the presence of other impurities. This latter statement is supported by the observation that using ultra-high purity starting powders resulted in a very different microstructure (compare Figures 3b and 3c). The relative values of surface and grain boundary energies, and how those are influenced by the presence of LiF must be extremely sensitive to the starting powder purity.

It is noteworthy that pore coalescence into roughly cylindrical shapes (e.g., Figure 5) occurred during the heat treatment in both the doped and un-doped spinel. It is readily shown that if the total pore volume is constant, the total surface area of a group of spherical pores is lower than the total surface area of cylindrical pores. Thus, the pore coalescence observed here seems to be going against the driving force to minimize the surface energy of the system. This apparent contradiction is likely due to the fact that the pores are located at grain boundaries, and the increase in surface area during coalescence

is accompanied by a decrease in grain boundary area. If LiF leaves the system during heat treatment, this may further increase the grain boundary energy. It is likely that the only reason pores coalesce during the heat treatment and not during hot pressing is that the applied stress in hot pressing provides a strong driving force to remove porosity. This indicates that unless the thermodynamics are altered by changing the relative grain boundary and surface energies, pressure during densification is necessary to obtain transparent spinel. Furthermore, extended exposure to high temperature would be expected to degrade the microstructure.

CONCLUSIONS

It has been demonstrated that the microstructure and transparency are extremely sensitive to the purity level of starting powder. In the present case, exceptional transparency was achieved only when the solution used to incorporate Mg into the boehmite structure contained a very high level of purity. The role of these impurities, which are presumed be in the parts per million range, is to alter the relative grain boundary to surface energies such that the driving force for pore evolution and/or removal is altered. Optimization of transparent spinel for optical, mechanical and corrosive properties will only be achieved by purposeful addition of impurities to alter the microstructural evolution. The latter will only be possible by fully understanding the role of impurities on the corresponding boundary and surface energies.

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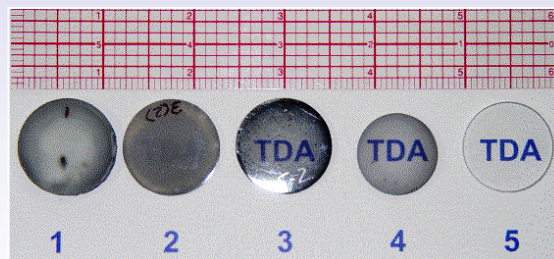


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Outline

- Background
- Experiments
- Optical Measurements
- Microstructure Characterization
 - As processed
 - After annealing
 - Sensitivity to impurities
- Conclusions



Improvements in
powder/processing methods

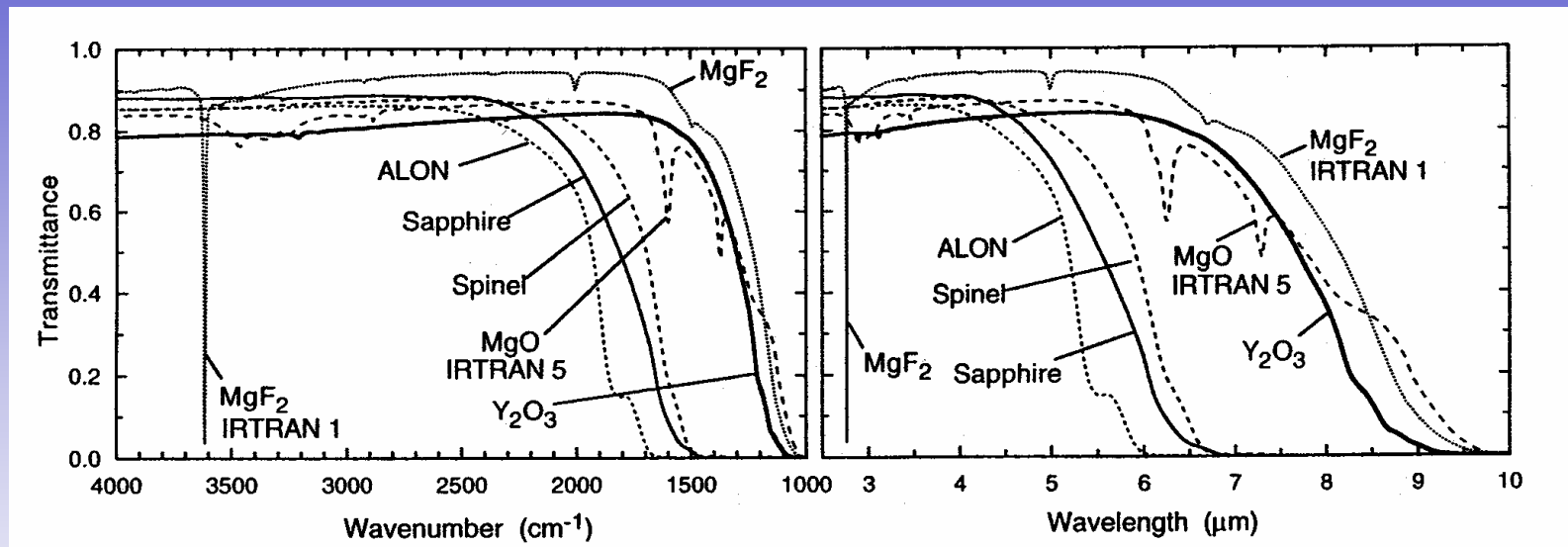


annealed sample



Background

● Transparency in Various Ceramics



From D.C. Harris, 1999

Spinel: no birefringence



MgAl₂O₄ Spinel is worth the effort

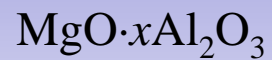
Absorption coefficient (cm⁻¹) of spinel, sapphire and ALON at 5 μm

Material	25 °C	250 °C	500 °C
Spinel	0.4	0.7	1.3
Sapphire	0.8	1.3	2.1
ALON	1.6	2.4	3.7

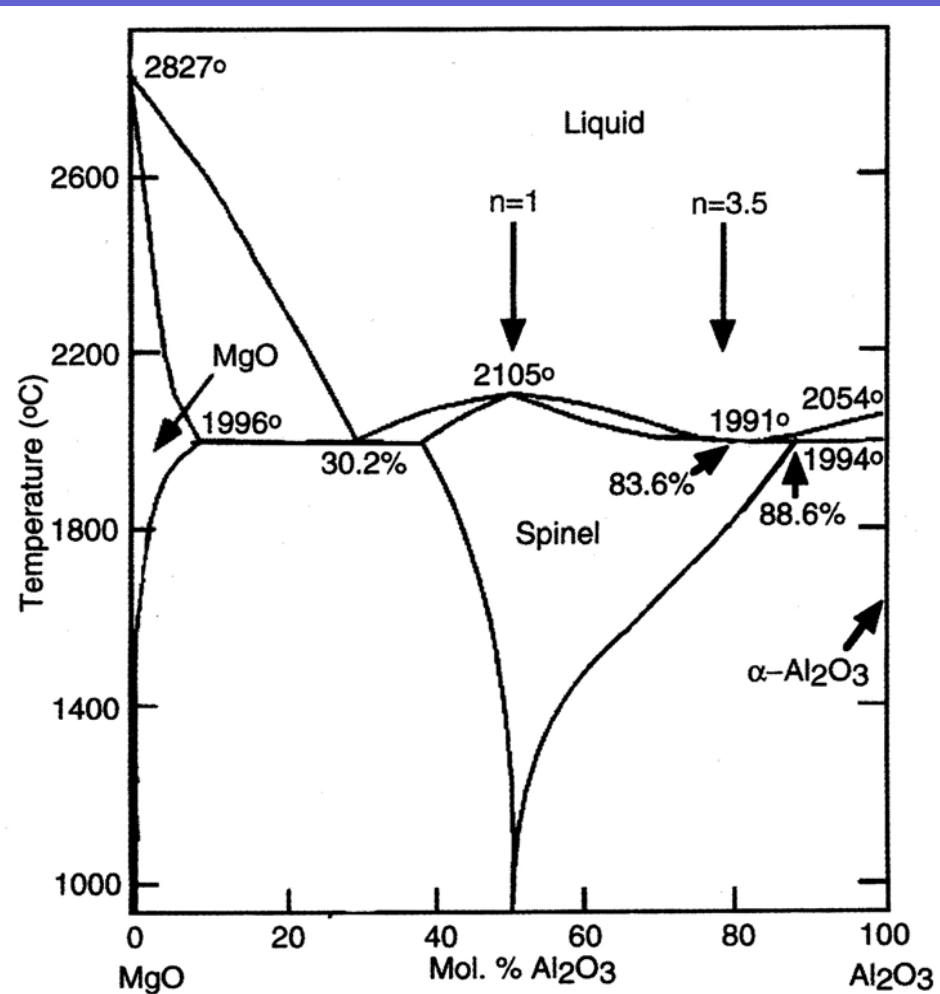
MgO-Al₂O₃ Phase Diagram

Background

Stoichiometric Range



$$0.6 < x < 7.0$$



adopted from Hallstedt



Experimental Conditions

● Spinel Powder Preparation

- TDA “Soft Chemical” Method
 - Room temperature metal exchange
 - Boehmite + carboxylic acids and Mg-acetylacetonates
 - Water based
 - Produces 40-70 nm particles
 - Metal exchange reaction
 - Surface modified boehmite plus $\text{Mg}(\text{acac})_2$
 - Heating above 500°C removes organics and gives $\text{Mg}/\gamma\text{-Al}_2\text{O}_3$
 - Heating above 900°C to gives MgAl_2O_4 spinel powder

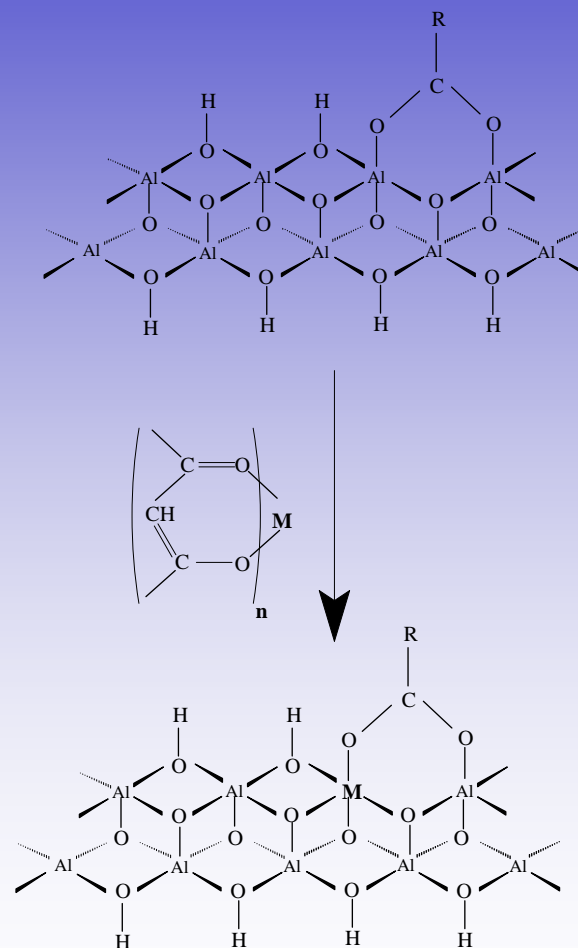
TDA Research



Generality of Metal Exchange Reaction

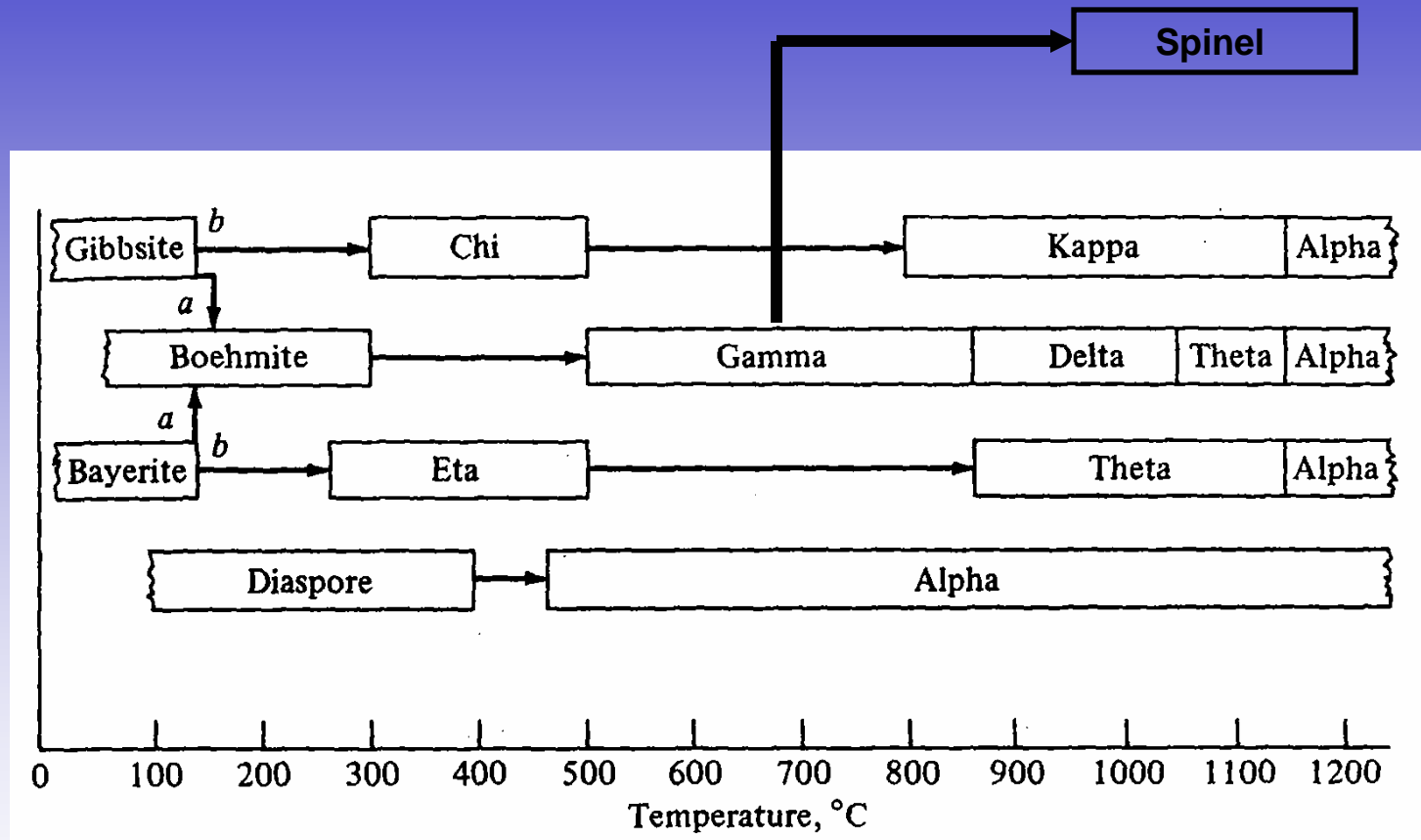
Experimental Conditions

- **Carboxylic acid modified boehmite promotes metal exchange reaction**
 - wide range of metals can be exchanged with aluminum cations (Li, Na, K, Mg, Ca, Sr, Ba, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Tc, Ag, Cd, In, Sn, Hf, Re, Hg, Pb, La, Ce, Nd, Pr, Th, or U)
 - multiple cations can be introduced
 - >+50% of Al^{3+} can be exchanged



Chemical Synthesis of Spinel

Experimental Conditions



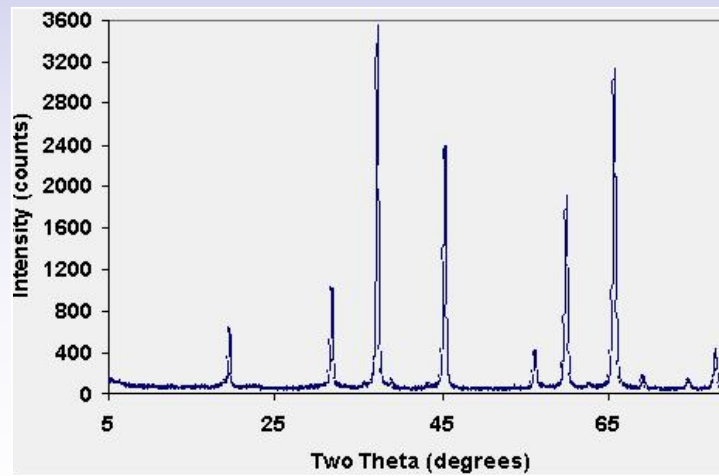
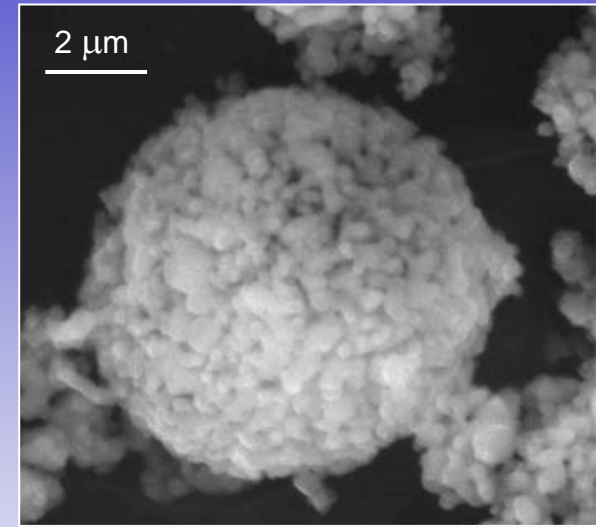
Spinel Starting Powder

Experimental Conditions

● Synthetic Advantages

- Precise doping control
- No aging effects
- Single phase products
- Single heat cycle
- Low temperature conversion due to nanoparticle formation
- Mixed powders easily formed
- Easy scale-up of reaction process

TDA; U.S. Patent 6,207,130

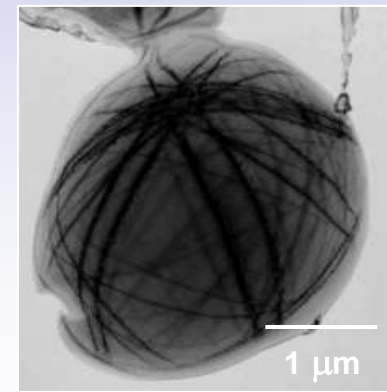


Spinel
powder



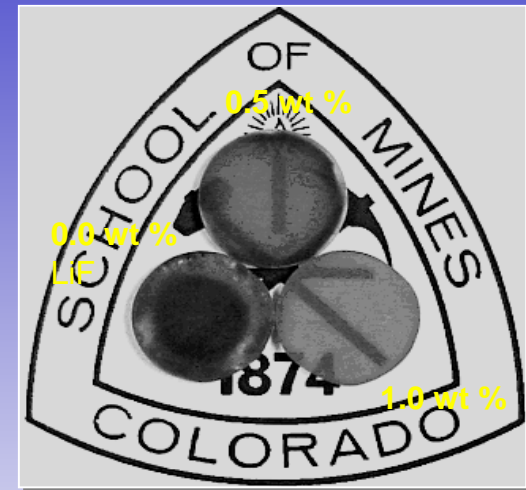
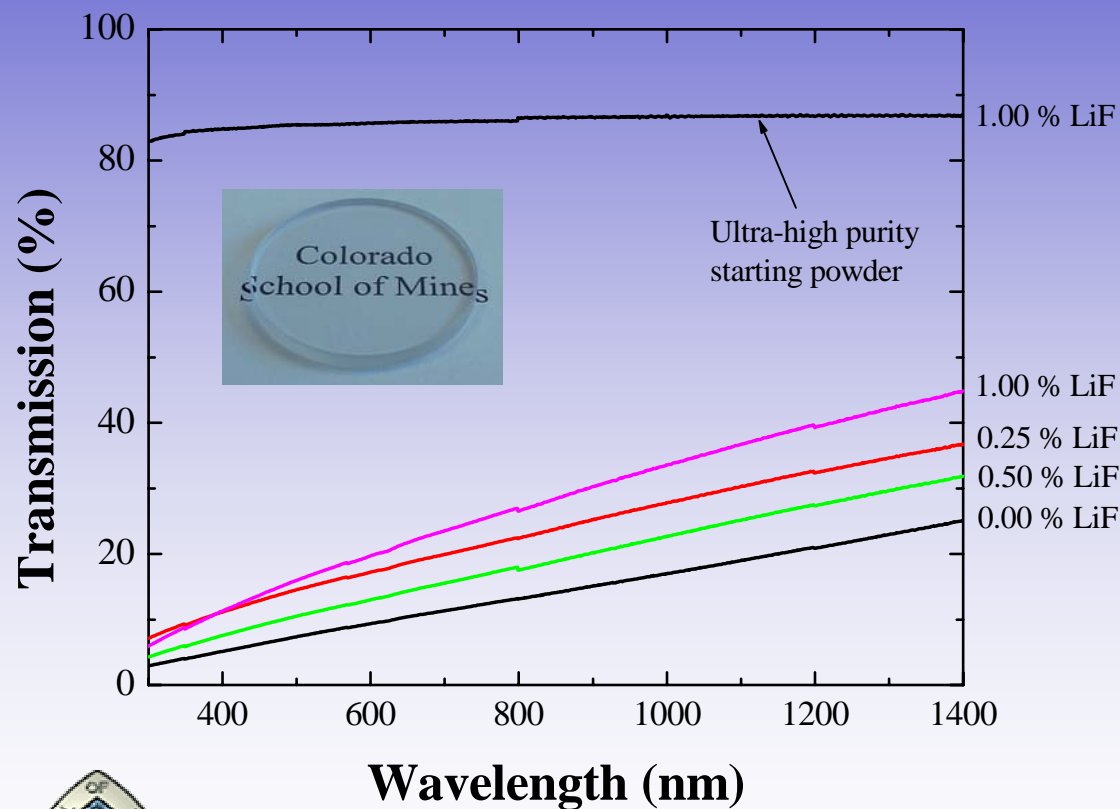
● LiF Additions, Hot-Pressing, Annealing

- Novel spinel powders produced by TDA were mixed, using alumina milling media, with varying LiF additions:
 - 0 wt %
 - 0.25 wt %
 - 0.5 wt %
 - 1.0 wt %
- Spinel powders were hot-pressed at 1550 °C in a graphite mold applying 35 MPa
- Upon hot-pressing, a separate set of samples was annealed at 1550 °C for 10 hours
- Microstructure characterization was performed by scanning electron microscopy (SEM) and preliminary transmission electron microscopy (TEM) studies



Optical Properties

● Transmissivity



- Correlation of LiF addition and transmissivity unclear
- Surface Reflection
- Impurity/Porosity Effects
- 1.0 wt % LiF exhibits highest transmissivity

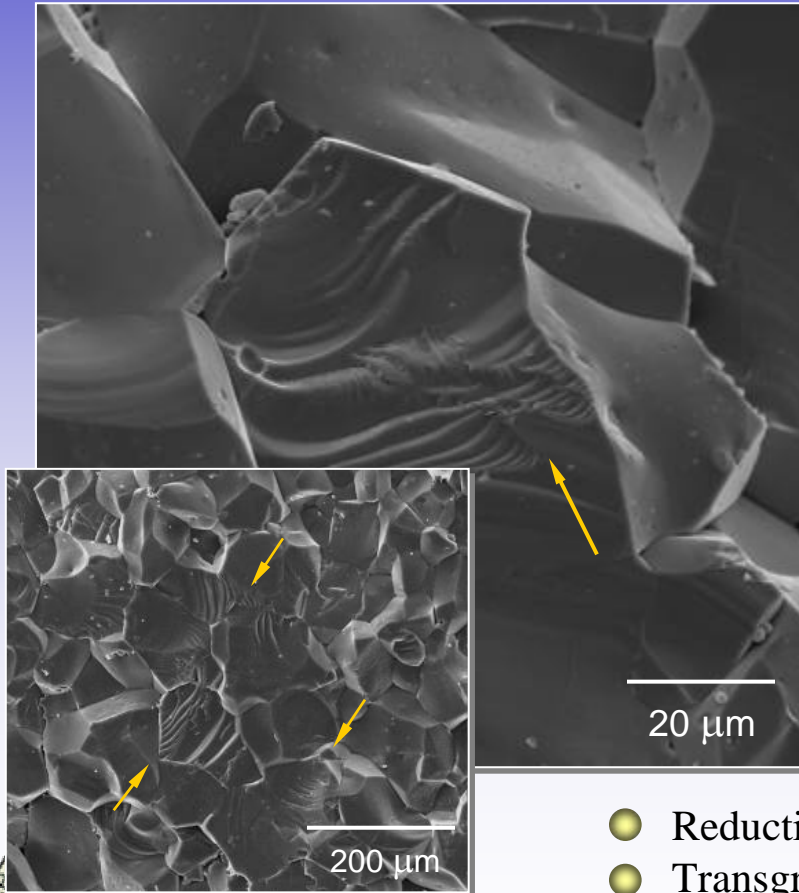


Fracture Surfaces

Microstructure Characterization

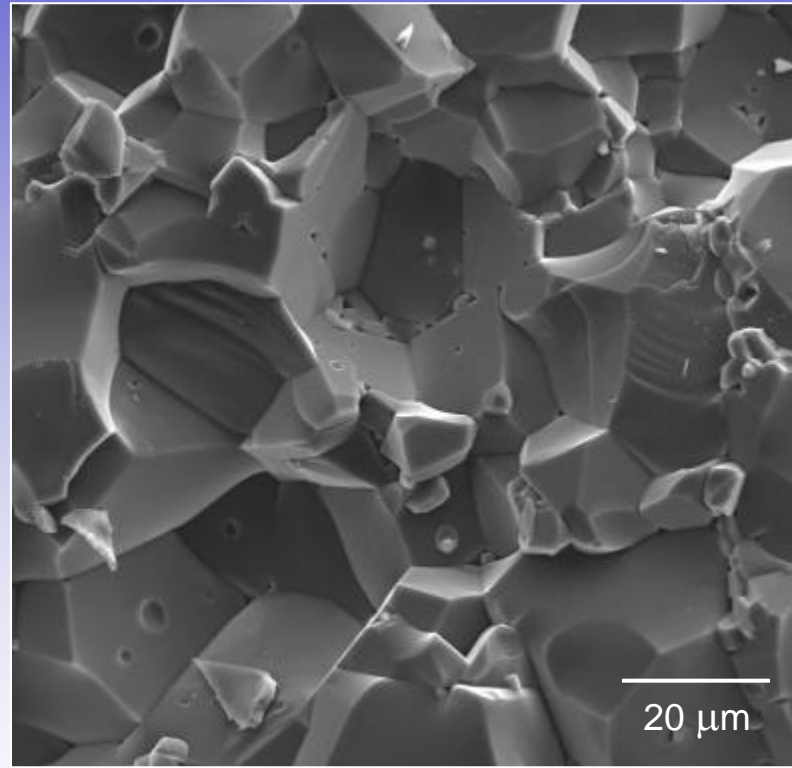
● As-Hot Pressed Samples

0.0 wt % LiF



SEM imaging

1.0 wt % LiF

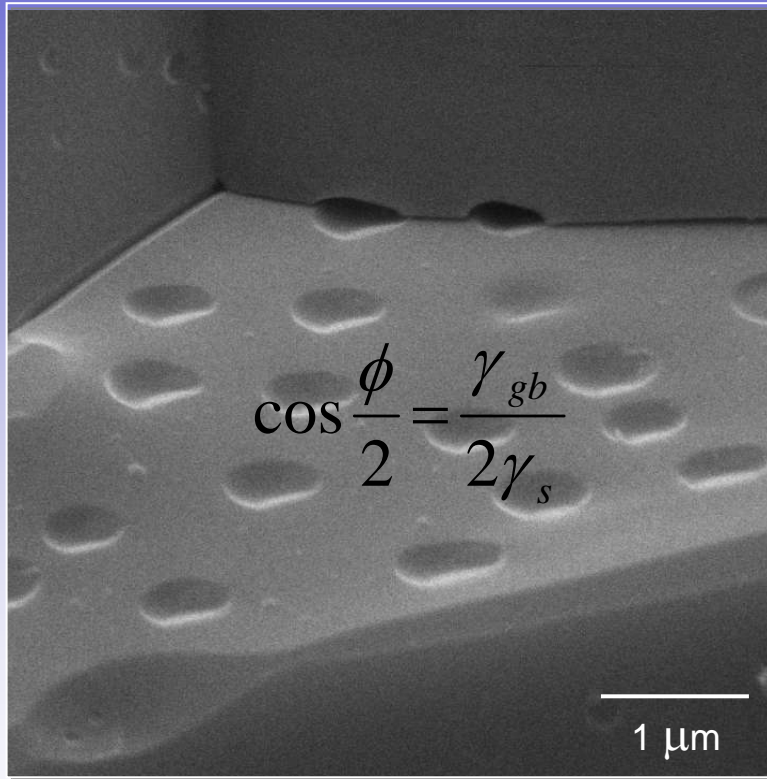


- Reduction in grain size (about a factor of 4x)
- Transgranular versus intergranular fracture mode

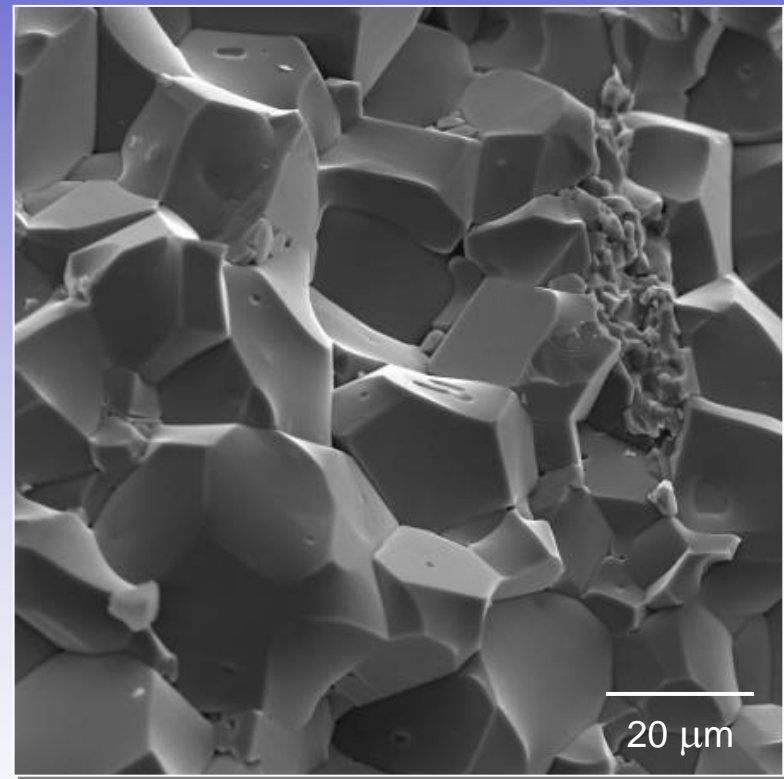


● As-Hot Pressed Samples

0.0 wt % LiF



1.0 wt % LiF



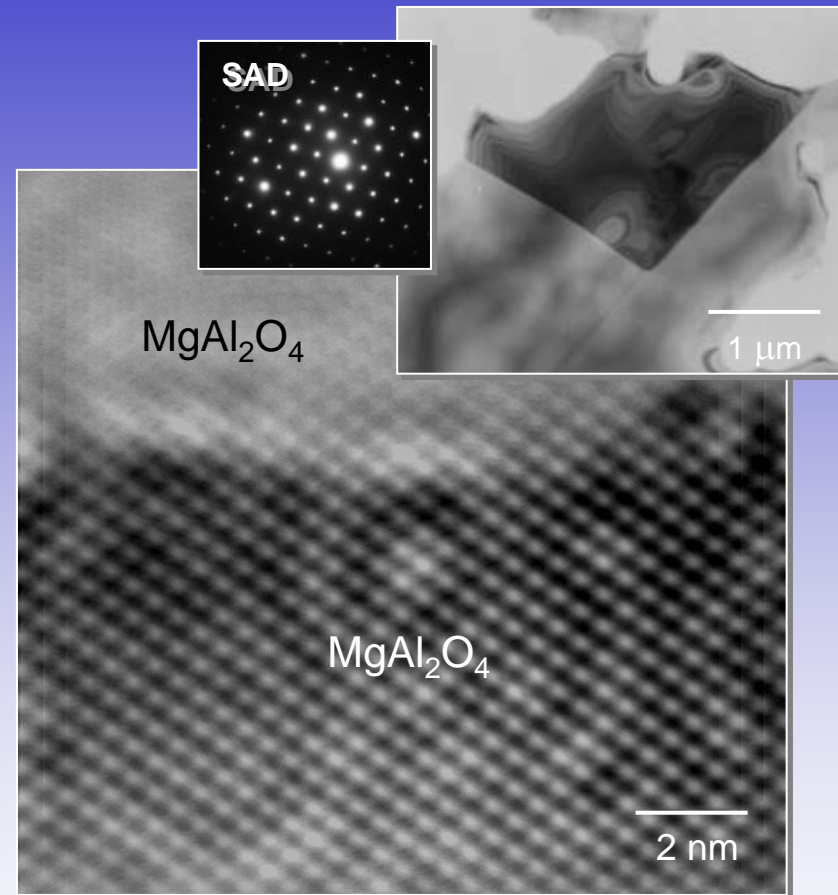
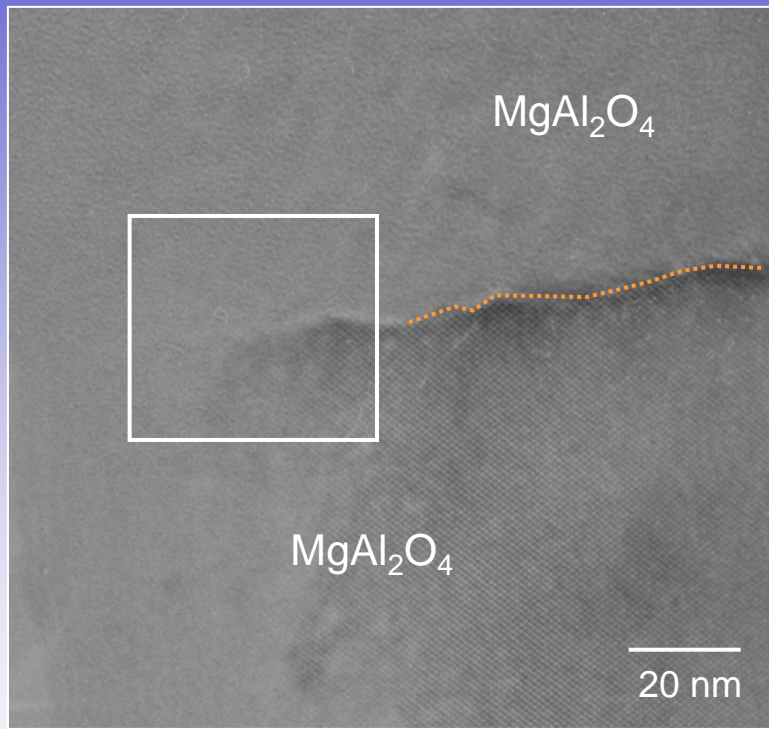
- No LiF additions results in a high fraction of residual pores at interfaces
- All pores observed resided at grain boundaries and triple junctions

Segregation of LiF?

TEM imaging

● Interface Characterization

1.0 wt % LiF



- Preliminary results of interface regions of the sample doped with 1.0 wt.% LiF showed no secondary phase formation or LiF segregation at interfaces but rather rough boundary planes

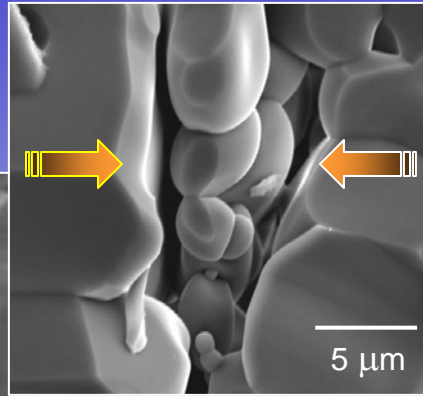
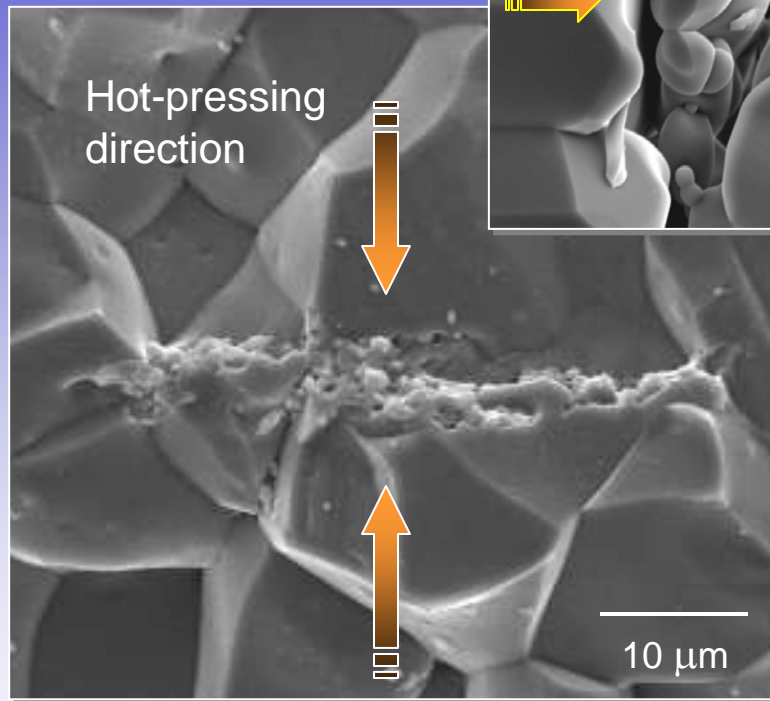


Fracture Surfaces

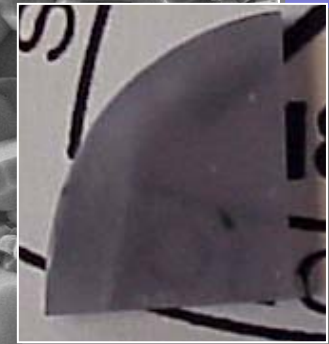
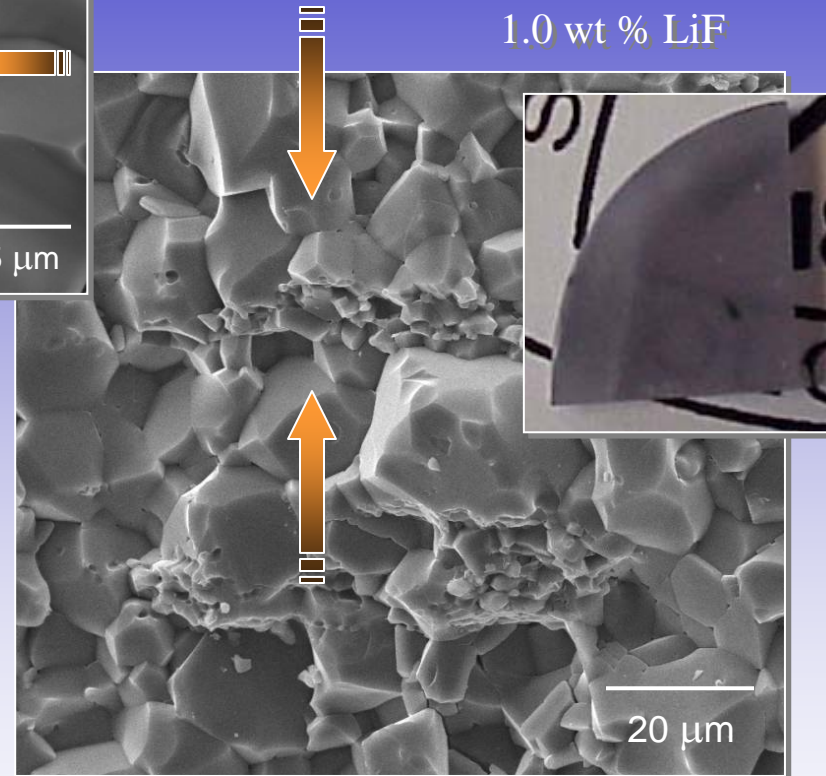
Problems Encountered

● LiF Mixing

0.25 wt % LiF



1.0 wt % LiF



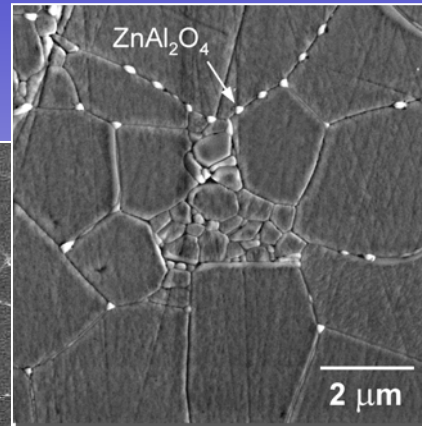
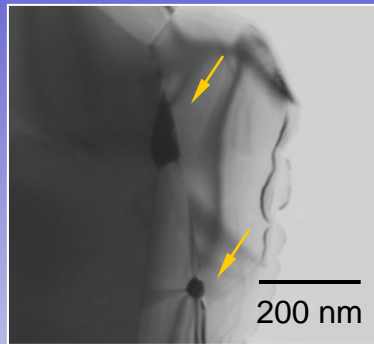
- SEM imaging suggests that mixing of LiF additions was non-uniform resulting in localized regions of reduced grain size perpendicular to the hot-pressing direction



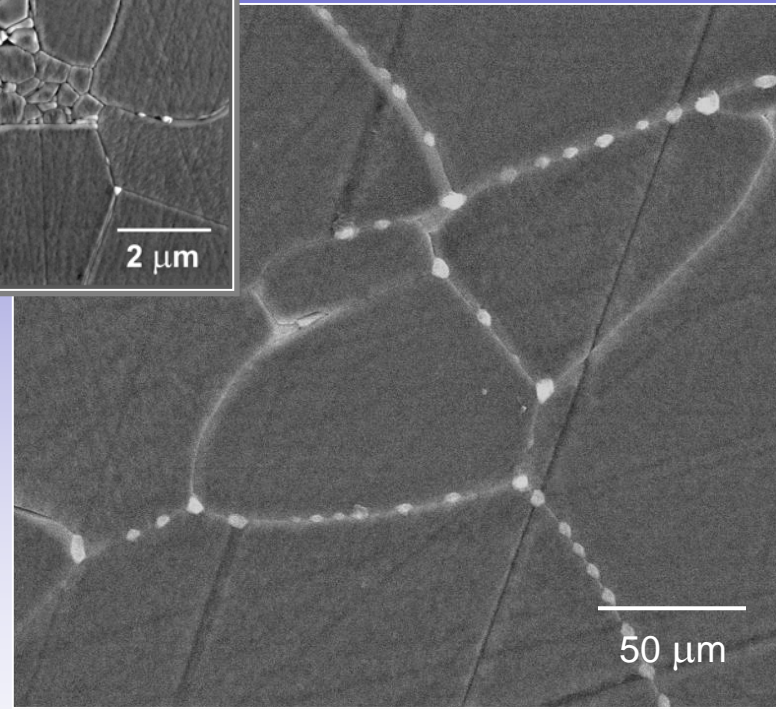
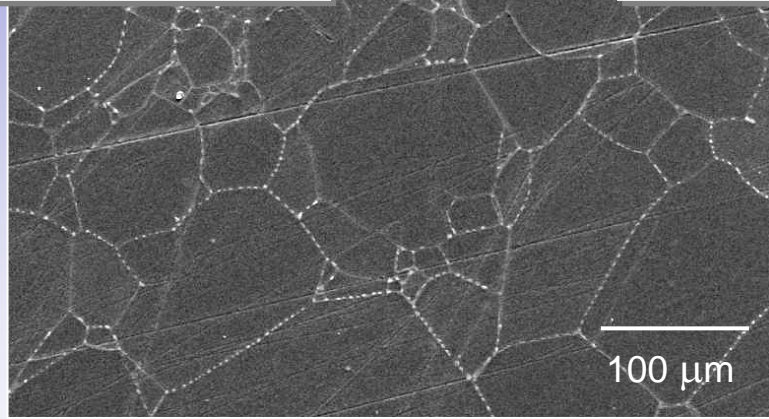
Polished Surfaces

Problems Encountered

● Powder Impurities



1.0 wt % LiF

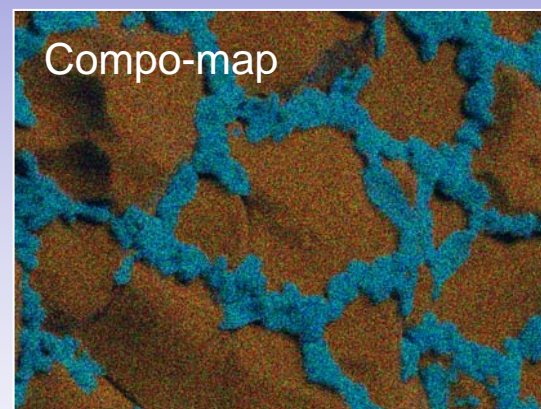
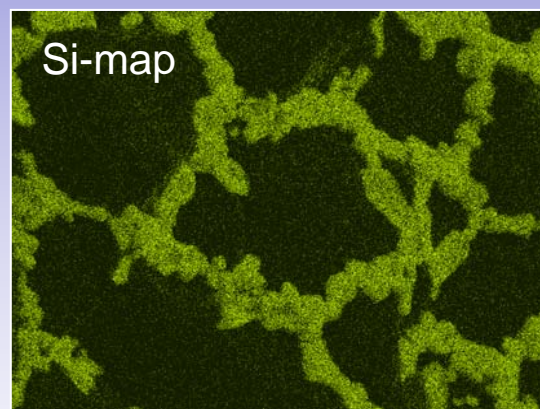
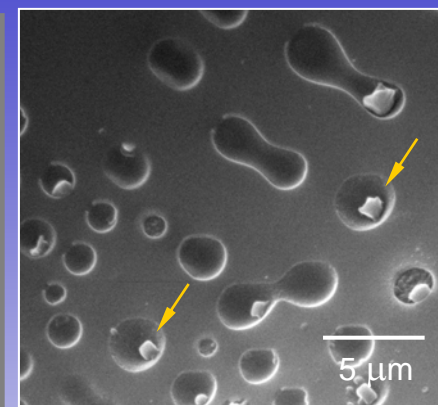
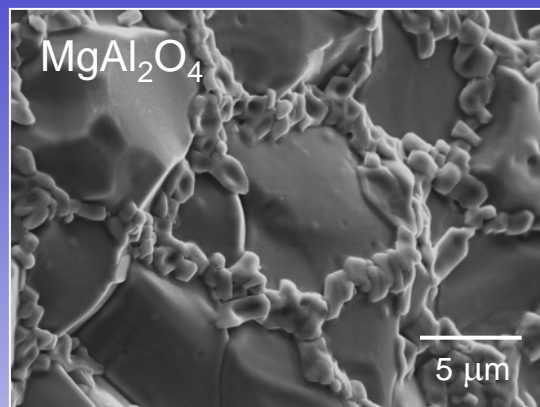
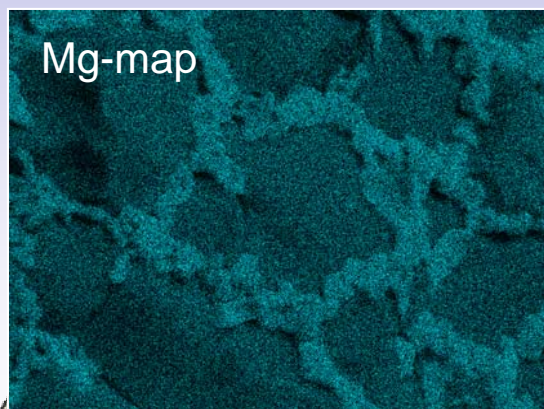
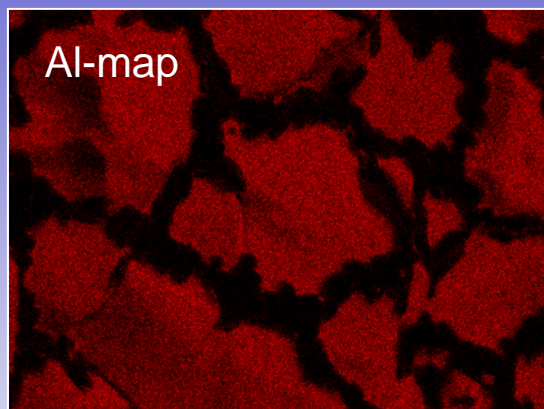


- The LiF starting powder ($\text{Mg}(\text{acac})_2$) contained a small fraction of Zn-contamination which led to the formation of nm-sized ZnAl_2O_4 spinel precipitates located at grain boundaries



Mg-Silicate Contamination During High Temperature Exposure

- **SEM Imaging**
EDX – elemental mapping



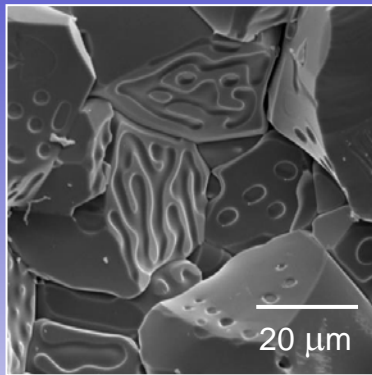
- Simultaneous acquisition of elemental maps of various elements
- Decoration of grain boundaries with a Mg-silicate



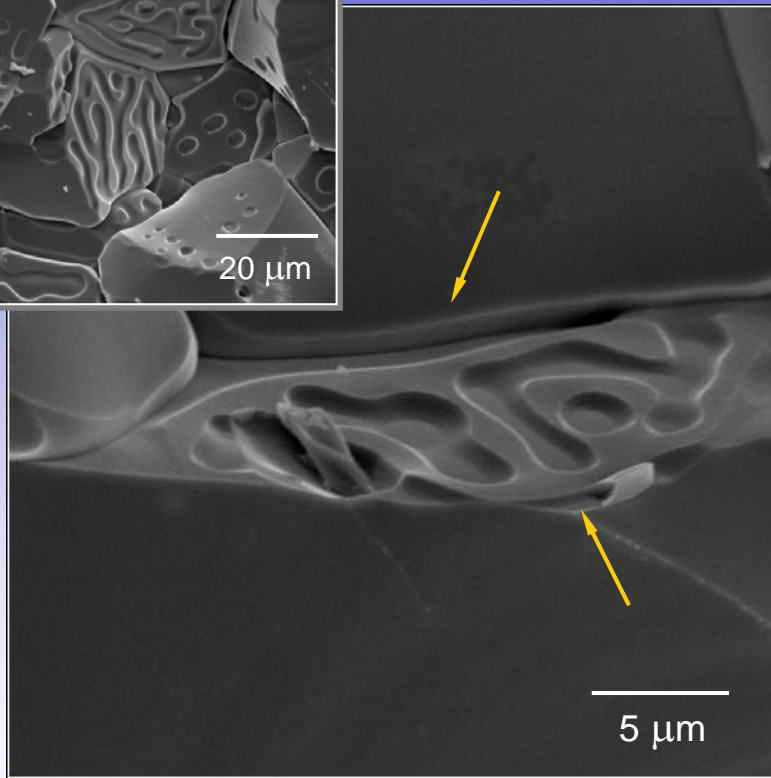
Fracture Surfaces

SEM Imaging

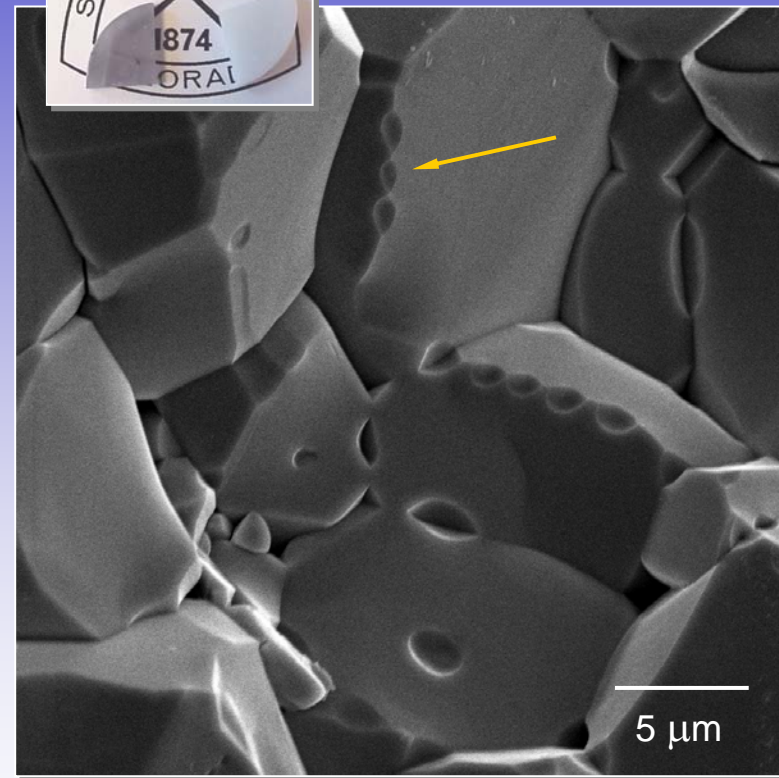
● Annealed Samples



0.0 wt % LiF

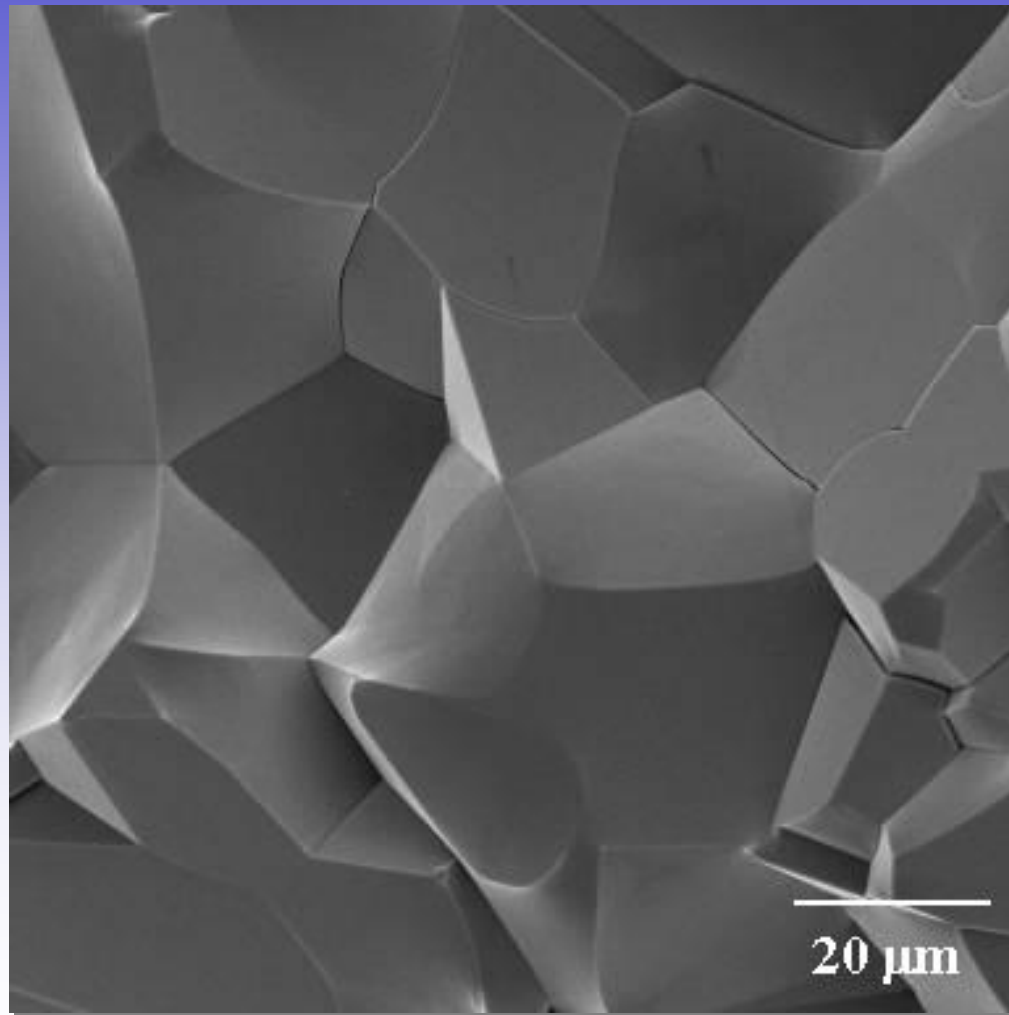


1.0 wt % LiF



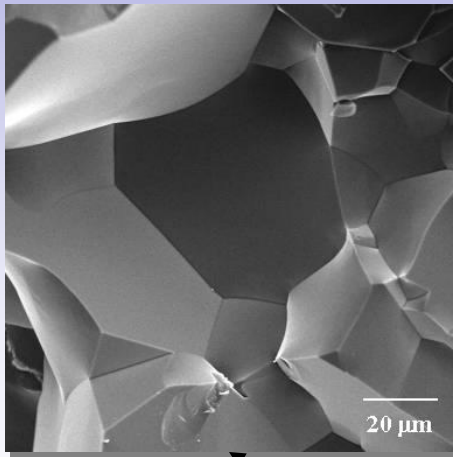
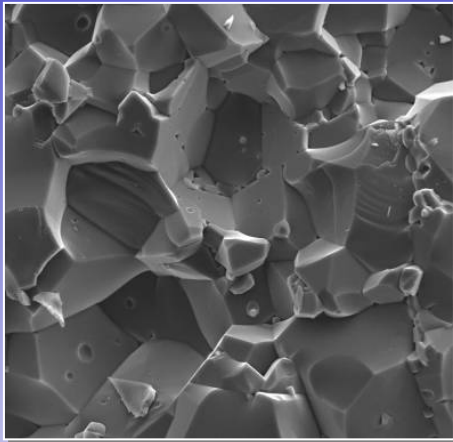
- With no LiF – pronounced coalescence of boundary pores and faceting
- With LiF – increased porosity, but reduced boundary coalescence and faceting

Ultra-high purity starting powder (removal of ppm impurities)



Fracture Surfaces

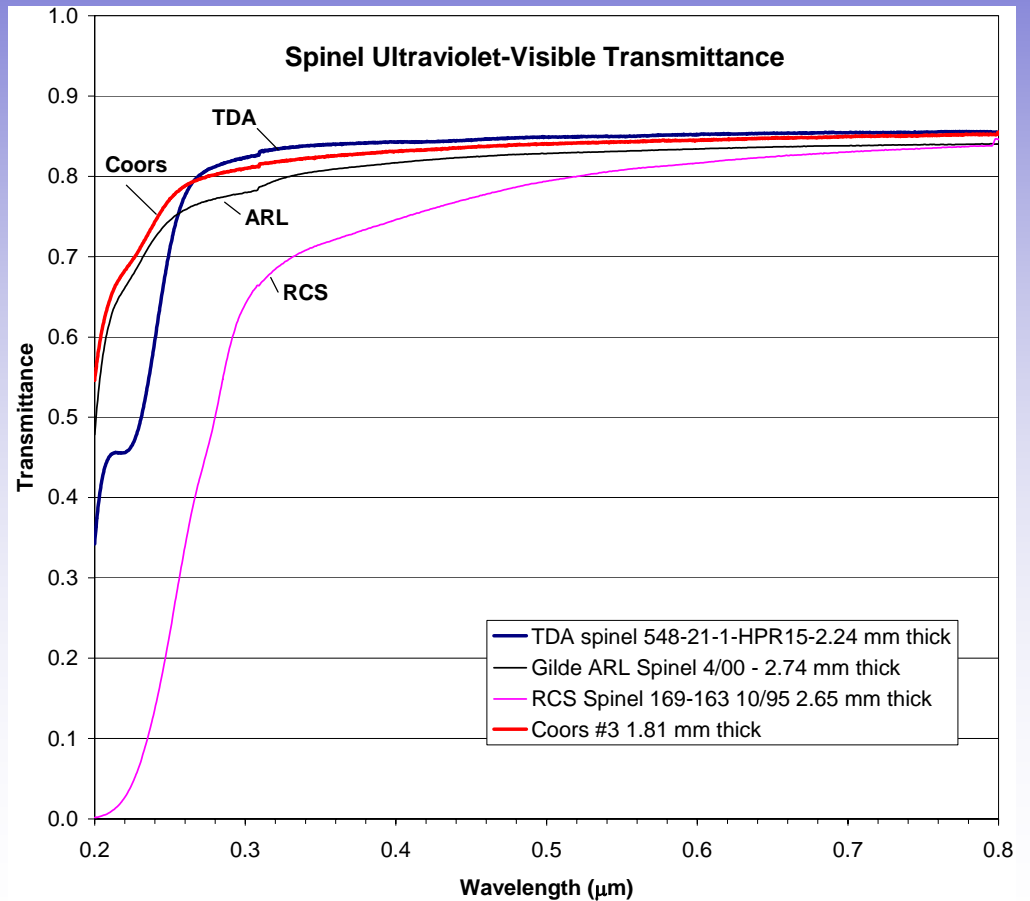
1.0 wt % LiF



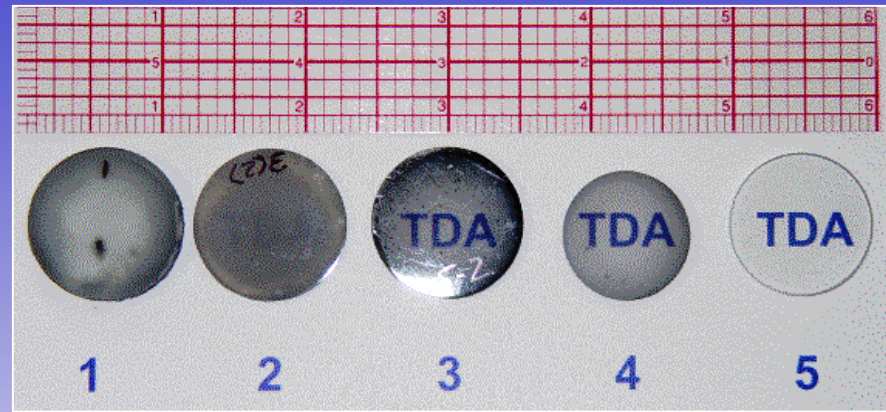
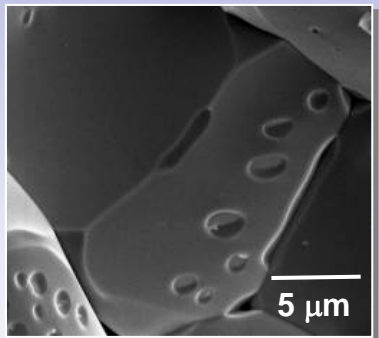
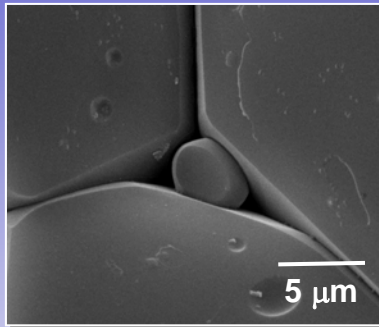
High Purity
Starting Powder

Starting Powder Purity

- Grain size an order of magnitude larger (up to 500 μm grain diameters)
- No porosity observed
- Unique grain boundary topography



Conclusion



Improvements in powder/processing methods

● Processing of Transparent Spinel Ceramics

- Highly sensitive process
- Challenging to reproduce
- Impurities play an important role
- Dispersion of LiF is essential
- Annealing leads to white discs

